Self-assembled Structure of Amphiphilic Polythiophenes with Asymmetric Electronic Structures and its Photovoltaic Properties

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Creating an energy gradient or cascade structure at the donor/acceptor interface is important for efficient photocurrent generation in organic photovoltaic devices.[1,2] For this purpose, the self-assembly of all-conjugated block copolymers is one of the intriguing approaches.[3] In this study, we synthesized an amphiphilic polythiophene-based diblock-copolymer consisting of a hydrophobic hexylthiophene block and a hydrophilic oligoether-substituted fluorinated thiophene block with a 10:1 ratio (**BP12** in Fig. 1). We also investigated its self-assembly, solid-state properties, and electronic structures in comparison with the homopolymers **P1** and **P2** and a random copolymer **RP12**.

A drop of a solution of **BP12** smoothly spread on the water surface and afforded a thin film after evaporation of the solvent. In contrast, such spreading behavior was not observed for **RP12**, suggesting that the diblock structure is essential for the amphiphilicity of **BP12**. Contact angle measurements suggest that the thin film formed a hydrophobic surface on one side and a hydrophilic surface on the other due to amphiphilic self-assembly at the air/water interface. XPS analysis revealed that the hydrophilic side has a higher fluorine density and thus has a higher ionization potential by 0.2 eV than the hydrophobic side. Due to the asymmetric electronic structure of the thin film, planar heterojunction devices based on the film and $PC_{61}BM$ showed significantly different photovoltaic characteristics depending on the direction of the film. These results highlight the applicability of all-conjugated block copolymers for engineering donor-acceptor interfaces.

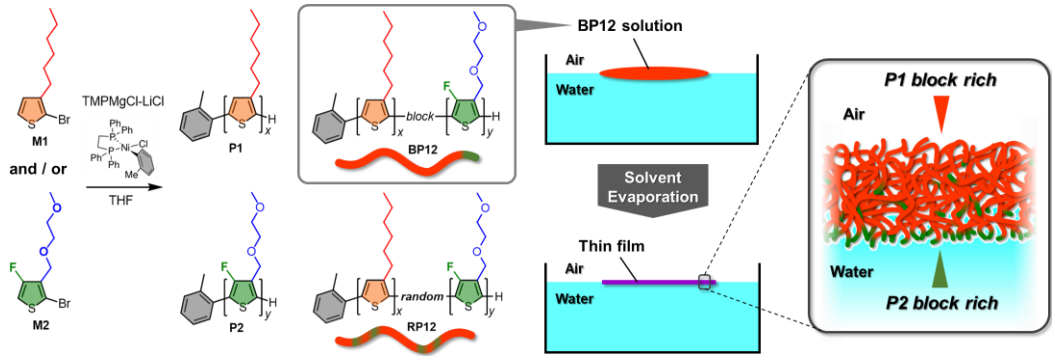

Fig. 1 Synthesis of homopolymers and block and random copolymers and schematic illustration of thin-film fabrication by the on-water-spreading method.

1) C. Groves, *Energy Environ. Sci.*, **2013**, 6, 1546. 2) S. Izawa et al., *Adv. Mater.*, 2015, *27*, 3025. 3) U. Scherf et al., *Acc. Chem. Res.*, **2008**, *41*, 1086.